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STEAM BOILERS, POWER-GENERATING FUEL, BURNERS, AND BOILER AUXILIARY EQUIPMENT

Generation and Reduction of Nitrogen Oxides in Firing Different Kinds of Fuel in a Circulating Fluidized Bed

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Abstract—The processes through which nitrogen oxides are generated and reduced in the course of firing different kinds of fuel in a circulating fluidized bed are addressed. All experimental studies were carried by the authors on their own laboratory installations. To construct a model simulating the generation of nitrogen oxides, the fuel combustion process in a fluidized bed was subdivided into two stages: combustion of volatiles and combustion of coke residue. The processes through which nitrogen oxides are generated and reduced under the conditions of firing fuel with shortage of oxygen (which is one of efficient methods for reducing nitrogen oxide emissions in firing fuel in a fluidized bed) are considered.

Keywords: nitrogen oxides, solid fuel, circulating fluidized bed

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The process through which nitrogen oxides are generated in a fluidized bed in the course of burning the particles of solid kinds of fuel was studied on an experimental setup made in the form of an electric furnace fitted with a cylindrical heating chamber with an inner diameter of 50 mm and an air distribution hood welded into the bottom. During the experiments, we checked the temperature of fluidized bed composed of 460-μm fractions of fused alumina (or ash particles 2.5 mm in size) and air flowrate. In addition, the composition of combustion products was continuously measured using different types of gas analyzers (GIAM-5 for CO_2, Bekman 951 A for NO_x, GIAM-5M for CO, and DET-V for O_2) and a computerized data acquisition and processing system. Brown coal from the Moscow region, Berezovo coal, Donetsk anthracite, Kuznetsk lean coal, undersized coke of Kuznetsk coal, Estonian shale, and Volga shale were used as fuel [1].

For carrying out the experiments, we sieved fuel fractions with particles having medium sizes of 0.8, 1.5, 2.5, 4, 6, and 8.5 mm; small-weight charges (0.5–2 g) were fired in the fluidized bed at different temperatures.

Experiments involving preliminary blowing of fluidized bed with air at a temperature of 900°C showed that so-called thermal nitrogen oxides (i.e., those generated from the molecular nitrogen contained in air according to Zeldovich' mechanism [2]) are not generated under the conditions of the experiment. In view of this, all generated nitrogen oxides were subsequently regarded as fuel ones, originated from the nitrogen contained in fuel.

The data shown in Fig. 1 illustrate how nitrogen oxides and carbon dioxide are generated in firing small-weight charges (0.5 g) composed of particles of coal from the Moscow region and anthracite. For all coals with a high content of volatiles, an interconnection between the changes of CO_2 and NO_x concentrations is observed: during the combustion of volatiles, a synchronous and very rapid growth of C_{NO} and C_{CO_2} concentrations takes place, and during the combustion of coke residue these concentrations decrease gradually to zero. If fuel with an insignificant content of volatiles is fired, the maximum of CO_2 and NO_x concentrations is not so prominent: nitrogen and carbon oxides are generated more uniformly. For quantitatively estimating the generation of CO_2 and NO_x, we calculated their relative masses m_{NO_x} and m_{CO_2}, that have released by a certain moment of time τ using the following expressions:

$$m_{NO_x}(\tau) = \frac{\int_0^{\tau} C_{NO_x} d\tau}{\int_0^{\tau_{b\text{-}o}} C_{NO_x} d\tau}; \quad m_{CO_2}(\tau) = \frac{\int_0^{\tau} C_{CO_2} d\tau}{\int_0^{\tau_{b\text{-}o}} C_{CO_2} d\tau},$$

where $\tau_{b\text{-}o}$ is the experimentally determined full time for which the fuel charge burns out.

At the combustion stage, nitrogen oxides are generated more intensely than CO_2. The relative fraction φ_N of nitrogen oxides released for the time of visible combustion of volatiles is a quantitative parameter using which this intensity can be estimated. Figure 2a shows this parameter as a function of the content of volatiles in the fuel.

It should be noted that the authors of the majority of proposed calculation procedures [3–5] postulate

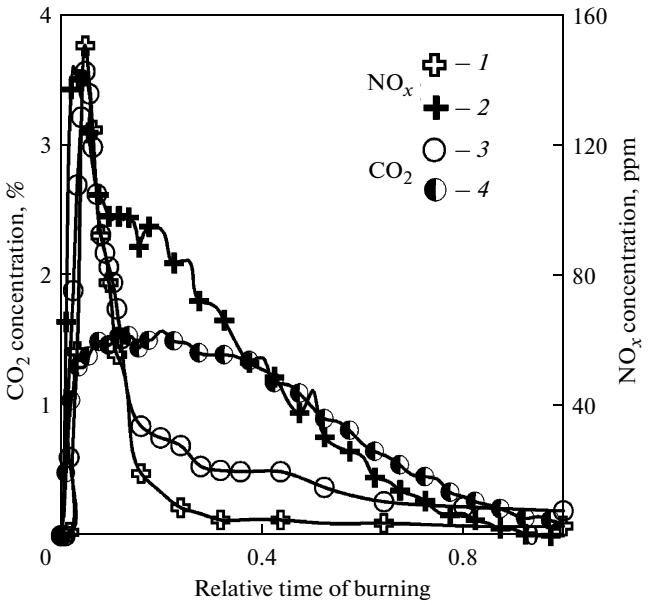

Fig. 1. Yield of CO_2 and NO_x during the combustion of coal from the Moscow region and anthracite. (*1*) and (*3*) Coal from the Moscow region, and (*2*) and (*4*) anthracite.

that nitrogen oxides are predominantly generated from volatiles assuming that the overwhelming majority of nitrogen containing compounds decompose during the release of volatiles. However, the obtained experimental data (see Fig. 2a) testify that it is incorrect to neglect with the generation of nitrogen oxides during oxidation of coal coke residue in the studied range of temperatures, especially for fuels with a low yield of volatiles.

In some works of Russian [6–8] and foreign [9–12] researchers, it is pointed out that a coal particle consists of intricate molecular complexes the atoms of nitrogen and carbon in which are closely linked with one another. During combustion, the molecular links are destroyed; the atoms of C and N are becoming free simultaneously and in certain proportions, and on reacting with oxygen, they finally produce CO_2 and NO_x in proportional amounts. Hence, the carbon combustion and nitrogen oxide generation processes must be considered jointly, and the mechanisms governing these processes should have much in common.

The data shown in Fig. 2b illustrate that the dependences of m_{NO_x} and m_{CO_2} on the relative time of combustion $\tau^*/\tau^*_{b\text{-}o}$ are almost identical with each other for the entire time of combustion of coal coke part (curves *1–4*) and volatiles (curve *5*). The value of $\tau^*/\tau^*_{b\text{-}o}$ varies from zero to unity; when the combustion of volatiles is considered, this parameter is understood to mean the relative time for which volatiles release and burn. The fact that curves *1* and *2* representing the yield of CO_2 and NO_x and constructed for coke residue and for preliminarily obtained semicoke of Kuznetsk coal, respectively, coincide with each other speaks in favor of the statement that there is good reason to consider the combustion process of real coals as consisting of two stages. During the combustion of volatiles (curve *5*), the CO_2 and NO_x generation rates are relatively low at the initial stage (the particle heating stage), and then gases begin to release intensely, the generation rates of which are higher than they are at the coke burning stage.

In view of the fact that the CO_2 and NO_x generation dependences are close to each other at different fuel combustion stages and that the volatiles and coke combustion processes are characterized by essentially different regularities, a conclusion was drawn during the investigation that the regularities pertinent to the nitrogen generation process should be studied separately for the coal particle volatiles and coke residue combustion stages.

GENERATION OF NITROGEN OXIDES IN BURNING COKE RESIDUE

In studying the coke residue burning process, we calculated the flow of carbon from the decrease (loss) of carbon mass with time. The loss of mass from unit surface was determined from the data of gas analysis carried out after the release of volatiles. In carrying out the calculations, we took into account the change in the diameter of burning particles and the coke particle superheating temperature, which reached a few hundred degrees at high air excess factors. Experimental data obtained in the range of fluidized bed temperatures from 400 to 900°C were processed, as a result of which the values of coefficients in the Arrhenius equation for carbon oxidation rate were obtained (Table 1).

A rigid proportional correlation is observed between the amounts of produced nitrogen and carbon oxides, testifying that the NO_x generation intensity depends on the combustion rate of coke residue carbon for all studied coals. This gives us grounds to consider the fuel nitrogen oxidation process as a heterogeneous reaction with participation of atomic nitrogen bound with hydrocarbons into integral molecular complexes, which proceeds in parallel with the carbon oxidation reaction. In this case, the flow of carbon oxides j_N from unit external surface of fuel particles can be written as follows:

$$j_N = \nu_N k_N C^S_{O_2},$$

where $\nu_N = 46/32$ is the stoichiometric ratio of the reaction $N + O_2 = NO_2$; k_N is the nitrogen oxide generation rate constant, m/s; $C^S_{O_2} = \dfrac{C_{O_2}}{1 + k_C/\alpha_d}$ is the oxygen concentration at the surface of coke particles, kg/m^3, determined by their burnout rate; k_C is the

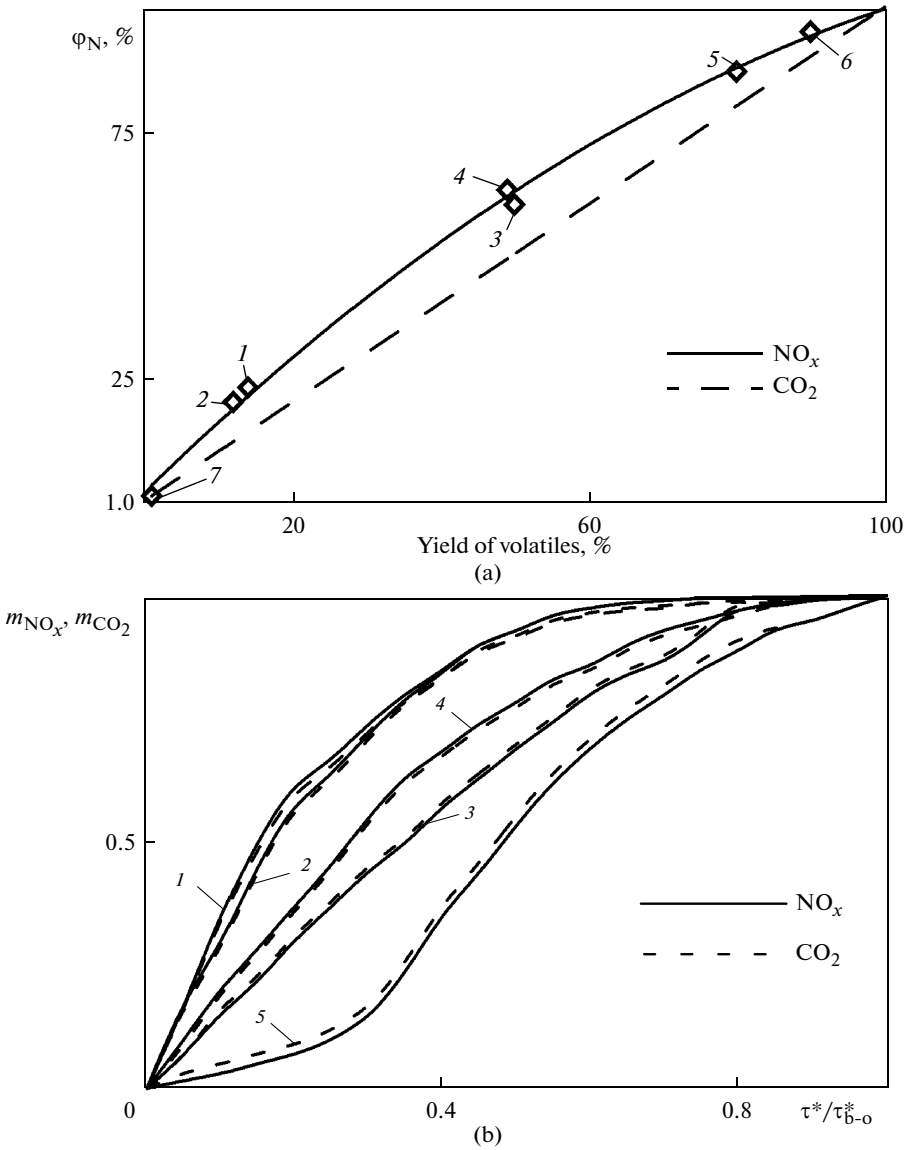

Fig. 2. The coefficient φ_N vs. the content of volatiles in the fuel and the CO_2 to NO_x yields ratio at the volatiles and coke residue burning stages. (a): (*1*) Kuznetsk coal, (*2*) Donetsk anthracite, (*3*) coal from the Moscow region, (*4*) Berezovo coal, (*5*) Volga shale, (*6*) Estonian shale, and (*7*) undersized coke. (b): (*1*) Coke residue of Kuznetsk coal, (*2*) semicoke of Kuznetsk coal, (*3*) coke residue of coal from the Moscow region, (*4*) coke residue of Berezovo coal, and (*5*) combustion of volatiles from Volga shale.

coke residue carbon oxidation rate constant, m/s; and α_d is the diffusion mass transfer coefficient, m/s.

For the k_N constant be calculated from experimental data, the particle's current size δ must be correlated at each moment of its burning time with the concentration of oxygen at the surface $C^S_{O_2}$, which is done in solving the traditional problem about the burnout of a single particle [13]. Since we are dealing with the kinetic characteristics of the nitrogen oxidation process k_N (and that of carbon k_C), we must take into account the superheating temperature T_s of burning fuel particles (which was calculated from the correlations presented in [14]) if we wish to calculate these characteristics accurately.

The obtained experimental data were subjected to processing, the results of which showed that the temperature dependence of the rate constant for the reaction in which the fuel coke part is oxidized by air oxygen is described by the Arrhenius equation (Fig. 3a)

$$k_N = k_N^0 \exp\left(-\frac{E_N}{RT_s}\right),$$

where k_N^0 is the exponent multiplier; E_N is the activation energy for the fuel nitrogen oxidation reaction, J/mol; and R is the universal gas constant.

It follows from Fig. 3a that the values of activation energy E_N, corresponding to the slope ratio of the dependences $\ln(k_N) = f(1/T_s)$, shown in the figure are

Table 1. The values of coefficients and activation energy in the Arrhenius equation for the carbon and nitrogen oxidation rate constants

Parameter	Fuel				
	coal from the Moscow region	Berezovo coal	anthracite	undersized coke	Kuznetsk coal
k_C^0, m/s	68700	39100	8700	8800	5500
E_N, kJ/mol	135	131	118	113	107
$\overline{k_N^0}$, m/s	6.50	9.64	11.34	20.39	40.56

almost equal to each other (the difference is around 2% and corresponds to the experiment accuracy). This means that the mechanisms governing the generation of nitrogen oxides in burning coke residue are the same for all of the considered kinds of coals. Therefore, in our further studies, we took the same value of E_N for all kinds of coals equal to $\overline{E_N} = \frac{1}{5}\sum_{i=1}^{5} E_{N_i} =$ 101507 J/mol. By averaging the experimental values of k_N at the average activation energy $\overline{E_N} = 101507$ J/mol, we obtained the values of the exponential multiplier $\overline{k_N^0}$ (see Table 1). It was found from processing of experimental data that the value of $\overline{k_N^0}$, is proportional to the content of nitrogen N_K^{daf} in the ash-free part of fuel coke residue (Fig. 3b).

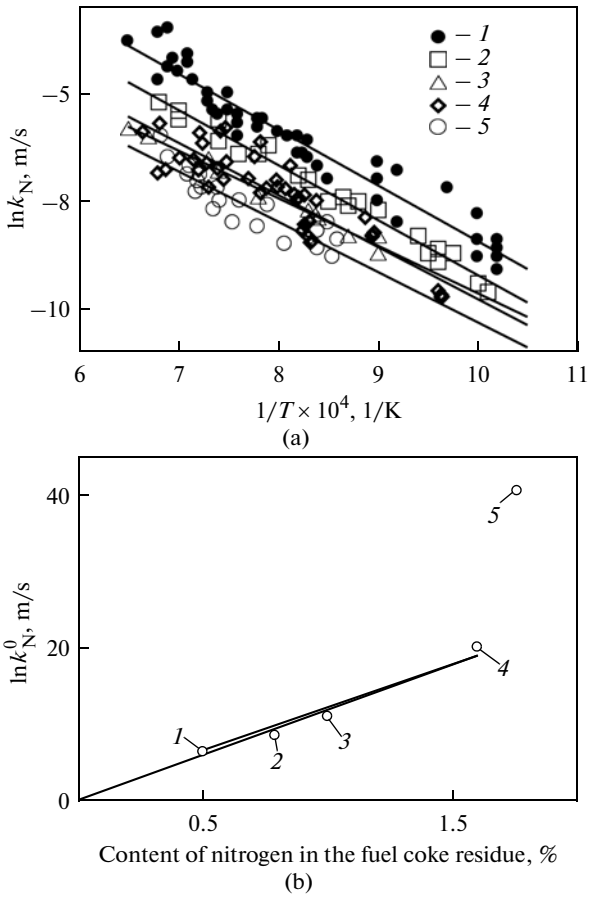

Fig. 3. Chemical reaction rate constant k_N vs. the particle temperature (a) and the exponent coefficient vs. the content of nitrogen in coke residue (b). (*1*) Kuznetsk coal, (*2*) undersized coke, (*3*) anthracite, (*4*) Berezovo coal, and (*5*) coal from the Moscow region.

GENERATION OF NITROGEN OXIDES DURING THE COMBUSTION OF VOLATILES

A model representing the release and burning of volatiles constructed taking into account variation of fuel particle temperature as a result of its heating was adopted as a basis for describing the nitrogen oxide generation process during the combustion of volatiles in a fluidized bed. The following expression for calculating the fraction of decomposed hydrocarbons was obtained from simultaneous solution of the particle heating equations and an Arrhenius-like kinetic dissociation equation:

$$N = 1 - \exp\left[-\int_0^{Fo} \varphi_v \exp\left(-\frac{F_v}{\theta}\right) dFo\right], \qquad (1)$$

where $\theta = \frac{T_p - T_{f.b}}{T_0 - T_{f.b}}$ is dimensionless temperature, T_p is the current temperature of fuel particle, T_0 is the initial temperature of fuel particle, and $T_{f.b}$ is the fluidized bed temperature.

Apart from the Biot and Fourier numbers (Bi and Fo), dimensionless complexes traditionally used in thermal engineering calculations, Eq. (1) contains the complex $\varphi_v = k_v r^2 / a_p$, defined as the ratio of the characteristic rate of the gasification process $k_v r$ (where k_v is the exponential multiplier for the hydrocarbon dissociation reaction and r is the particle radius) to the heat wave propagation velocity a_p/r (where a_p is the fuel particle thermal diffusivity) and the Arrhenius criterion $F_v = E_v/(RT_{f.b})$, where E_v is the activation energy for the hydrocarbon dissociation reaction. By processing experimental data, we

Table 2. The values of quantities appearing in expression (4) for different kinds of fuel

Parameter	Coal		Shale	
	from the Moscow region	from the Berezovo field	Estonian	from the Volga region
k^0_{NV}, m^3/kg	168.0	523.0	101.0	21.6
E_{NV}, MJ/mol	16.87	30.30	11.52	12.66
$N^r \varphi_N/100$, %	0.162	0.400	0.045	0.595
$\overline{k^0_{NV}}$, m^3/kg	90	47	110	20

obtained the values of the kinetic characteristics describing the pyrolysis process.

It was found from the experiments on firing fuel having a significant content of volatiles that the fraction of nitrogen from volatiles that transfers into oxides ψ_v is almost independent on the blow velocity, i.e., on the time for which the gases dwell in the fluidized bed. This testifies that nitrogen-containing volatile compounds react with oxygen quite rapidly, and the process can be considered in a first approximation as an equilibrium one.

We assume that the resulting gas-phase reaction through which "volatile" nitrogen interacts with air oxygen is a first-order one both in nitrogen and oxygen. Considering that the NO_x generation rate is limited only by the velocity at which "volatile" nitrogen enters into fluidized bed, i.e., by the release rate of volatiles determined from expression (1), and assuming that the oxidation reaction itself proceeds rapidly enough, we write the formula for calculating the equilibrium constant of this reaction:

$$K^0_N = \frac{C_{NO_x}}{C_{N^{vol}} C_{O_2}}. \quad (2)$$

The concentration of "volatile" nitrogen can be found from the following formula:

$$C_{N^{vol}} = \frac{dN(\tau)}{d\tau} \frac{N^r \varphi_N \rho_0}{10000G} V_p, \quad (3)$$

where V_p is the particle volume, ρ_0 is the particle initial density, τ is time, and N^r is the content of nitrogen in fuel in the working state.

The values of K^0_N can be calculated from (1)–(3) with the CO_2 and NO_x concentrations known from an experiment as a function of fluidized bed temperature at each moment of time. It has been found from processing of experimental data that a dependence of the equilibrium constant K^0_N of the resulting nitrogen generation reaction on the fluidized bed temperature $T_{f.b}$ of the following form is observed at the volatile burning stage:

$$K^0_N = k^0_{NV} \exp\left(-\frac{E_{NV}}{RT_{f.b}}\right). \quad (4)$$

The coefficient k^0_{NV} and the activation energy of the reaction in which the nitrogen of fuel is oxidized by air oxygen E_{NV} calculated by approximating the experimental points using the least squares method are given in Table 2.

The average value of activation energy $\bar{E}_{NV}$ for shales is equal to 12.1 MJ/mol. To reveal the factors affecting the equilibrium constant, we obtained new values of the coefficient $\bar{E}_{NV}$ by averaging the experimental values at the average value of activation energy $\overline{k^0_{NV}}$, which are also entered in Table 2 for each of the considered kinds of fuel.

It was found in the course of data processing that there is a correlation between the reduced values of the exponential multiplier $\overline{k^0_{NV}}$ and the fraction of fuel nitrogen (in the working state) that releases together with volatiles ($N^r\varphi_N/100$). This dependence is satisfactorily approximated in the considered range of nitrogen content in fuel by a straight line. However, for kinds of fuel with a significant scatter of N^r, it is more reasonable to approximate experimental values of $\overline{k^0_{NV}}$ by a hyperbolic function of the form

$$\overline{k^0_{NV}} = 0.94\left(N^r \frac{\varphi_N}{10000}\right)^{-0.667},$$

where the complex $N^r \frac{\varphi_N}{10000}$ is a dimensionless quantity.

MODELING THE NITROGEN OXIDE GENERATION PROCESS IN A FLUIDIZED BED

Below, we consider the nitrogen oxide generation process with a view to determine the extent (ratio) to (at) which the nitrogen of fuel converts into oxides during the combustion of coke residue. An expression for the change of nitrogen oxide concentration along the height of a stationary fluidized bed resulting from oxidation of coke residue nitrogen can be written in

accordance with the mass action law for a heterogeneous reaction in the form

$$udC_{NO_x}/dh = \nu_N C_{O_2}^S k_N S, \quad (5)$$

where u is the air velocity reduced to real conditions, m/s, and h is the fluidized bed current height, m.

Integrating expression (5) for an exponential distribution of oxygen concentration along the bed height, we can obtain the expression for calculating NO_x concentration at the bed outlet

$$C_{NO_x} = \nu_N C_0 \frac{k_N}{k}\frac{1}{\alpha}, \quad (6)$$

where α is the air excess factor, m^3/kg.

This expression is valid only for the oxidation reactions $C \rightarrow CO_2$ and $N \rightarrow NO_x$ and takes into account, first, the properties of fuel (in the form of nitrogen and carbon oxidation reactions rate constants) and, second, the combustion process parameters.

The expression for the fraction in which the fuel nitrogen contained in coke residue ψ_c converts into oxides can be written as follows:

$$\psi_c = \frac{14}{46} G_{NO_x} \frac{100}{BN^r},$$

where $G_{NO_x} = \alpha V^0 B C_{NO_x}$ is the mass flowrate of the generated nitrogen oxide, kg/s; B is the fuel flowrate, kg/s; and V^0 is the theoretically necessary amount of air, m^3/kg.

Then, taking expression (6) into account, we obtain the equation for calculating ψ_c during the combustion of coke residue

$$\psi_c = \frac{14}{32} C_0 V^0 \frac{k_N}{k}\frac{100}{N^r}. \quad (7)$$

In determining the total ratio at which fuel nitrogen converts into oxides during the combustion of fuel with a significant content of volatiles, we should calculate the average concentration of oxygen in the bed from a formula that takes into account partial consumption of oxygen for oxidation of the volatiles. The expression for calculating the ratio at which fuel nitrogen converts into oxides ψ_v must be transformed taking into account the dependence for the concentration of volatile nitrogen oxides NO_x generated during the combustion process on the concentration of "volatile" nitrogen C_N^{vol} and the average concentration of oxygen in the bed $\bar{C}_{O_2}$:

$$C_{NO_x} = C_{N^{vol}} \bar{C}_{O_2} \frac{K_1}{(N^r \varphi_N/10000)^{0.667}},$$

where $K_1 = 0.94 \exp\left(\frac{\bar{E}_{NV}}{RT}\right)$ is a complex that depends only on the bed temperature.

The concentration C_N^{vol} of nitrogen-containing volatiles releasing during the firing of fuel that hypothetically contains combustible substances only in the form of volatiles can be determined (in recalculation for atomic nitrogen) from the expression

$$C_{N^{vol}} = \frac{N^r B}{100G} = \frac{N^r}{100\alpha V_v^0},$$

where G is the flowrate of gases, m^3/s.

Bearing in mind that the flowrate of generating nitrogen oxides G_{NO_x} is interrelated with their current concentration C_{NO_x} and fuel flowrate by the expression $G_{NO_x} = \alpha V_v^0 B C_{NO_x}$, we come to the following formula:

$$\psi_v = \frac{14}{46}\frac{273}{T_{f.b}} \bar{C}_{O_2} \frac{K_1}{(N^r \varphi_N/10000)^{0.667}}.$$

Taking (as a first approximation) that the oxygen concentration is distributed along the bed height in a pattern close to an exponential law also during joint combustion of the volatiles and coke, we find the expression for the conversion ratio:

$$\psi_v = \frac{14}{46}\frac{273}{T_{f.b}} \frac{C_0 K_1}{\{(\alpha[\ln\alpha - \ln(\alpha - 1)]\}(N^r \varphi_N/10000)^{0.667}},$$

where C_0 is the initial concentration of oxygen at standard temperature and pressure, kg/m^3.

The overall fuel nitrogen conversion ratio ψ into oxides during the combustion of fuel with a certain yield of volatiles V^{daf} is written as the following sum that takes into account the fraction φ_N of nitrogen oxides releasing together with volatiles:

$$\psi = \psi_c(1 - \varphi_N/100) + \psi_v \varphi_N/100. \quad (8)$$

GENERATION OF NITROGEN OXIDES DURING COMBUSTION WITH A SHORTAGE OF OXYGEN

The emissions of nitrogen oxides generated during the combustion of fuel in a circulating fluidized bed can be decreased considerably by organizing a two-stage process, according to which fuel is fired in the volume of fluidized bed itself with a shortage of air [6, 10, 15–19].

To elucidate the regularities pertinent to generation of nitrogen oxides in fluidized bed at shortage of air, we carried out experiments in which significant-weight charges (from 13 to 50 g) of anthracite were fired using the experimental installation described above. The bed height was increased in these experiments from 100 to 180 mm.

The results obtained from these experiments showed that the use of larger-weight charges resulted in a smaller relative concentration of NO_x, first, due to a shortage of oxygen as a reagent participating in the NO_x generation process according to the oxidation reaction and, second, due to reduction of the generated oxides on the coke surface [20–31].

According to the experimental data (Fig. 4), a peak of NO_x concentration is observed in the initial stage of

combustion; this peak is associated with the release of volatiles, which are contained in the anthracite, although in small quantities. The NO_x peak value is inversely proportional to the charge mass, which in all likelihood testifies that reduction of oxides generated from volatile nitrogen-containing compounds is taking place. In firing 25- and 30-g charges, generation of CO was observed only at the volatile release moment, and it was noted that the concentrations of CO and NO_x reached their maximal levels simultaneously. In firing 50-g charges of particles, CO is generated both at the volatile release moment and during the combustion of coke residue. In the latter case, if there is CO, the NO_x concentration drops to almost zero and then increases again. The experimental data were processed for the time interval of NO_x concentration measurements after the release of volatiles when the concentration of CO in the flue gazes was equal to zero. The results from this processing showed that the total fuel nitrogen conversion ratio ψ into oxides during the firing of anthracite particles in a bed with a temperature of 850–900°C decreases with increasing the charge mass. The value of ψ was calculated taking the experimental data into account from the following expression:

$$\psi = \frac{14}{46}\frac{G\times 100}{N^r m_0}\int_0^{\tau_{b\text{-}o}} C_{NO_x} d\tau, \qquad (9)$$

where $\tau_{b\text{-}o}$ is the fuel charge full burning time.

As follows from expression (7), the value of ψ during the combustion of coke residue does not depend on oxygen concentration. Therefore, the fact that ψ decreases with increasing the charge mass confirms the conjecture that generation of NO_x in fluidized bed is inhibited as the concentration of volatiles increases [24–27].

We now write the differential equation describing the change in the concentration of nitrogen oxides along the fluidized bed height resulting from their generation due to oxidation of fuel nitrogen and decrease of their quantity as a result of reduction at the surface of coke particles:

$$u\frac{dC_{NO_x}}{dh} = \nu_N k_N C^S_{O_2} S_r - k^r_{NO_x} C_{NO_x} S_r, \qquad (10)$$

where u is the velocity of gases under real conditions, m/s; $k^r_{NO_x}$ is the rate constant of the equivalent NO_x reduction reaction on the surface of coke particles, which conditionally replaces the entire set of complex reactions that in reality proceed near the particle and on its surface; and S_r is the specific reaction surface, which is calculated from the expression

$$S_r = \frac{6\rho_{in}(1-\varepsilon)z}{\rho_c \delta},$$

where z is the concentration of coke particles in the bed, ε is the porosity, ρ_c is the coke density, and ρ_{in} is the density of the bed inert material.

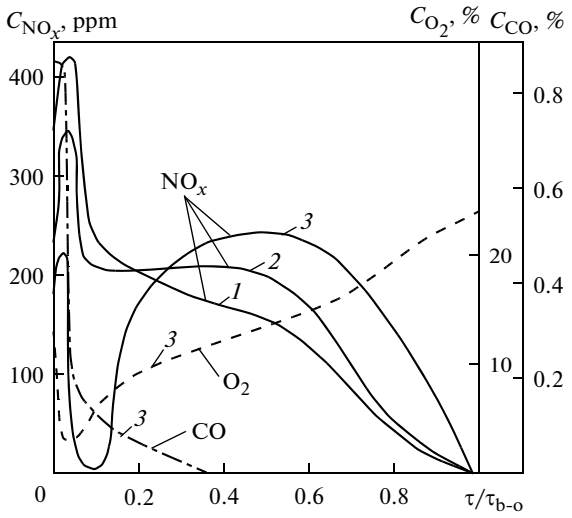

Fig. 4. Generation of nitrogen oxides during the fluidized bed combustion of anthracite with a shortage of oxygen. (*1*) Charge mass is 13 g, the diameter is 8.5 mm, and the bed temperature is 850°C; (*2*) charge mass is 30 g, the diameter is 4 mm, and the bed temperature is 900°C; and (*3*) charge mass is 50 g, the diameter is 4 mm, and the bed temperature is 900°C.

By integrating dependence (10) taking into account the exponential distribution pattern of oxygen concentration along the bed height and the constants $\bar{k}^0_N = f(T_s)$ and $k^0_C = f(T_s)$ calculated above (see Table 1), we can calculate the reduction constant $k^r_{NO_x}$ as a function of particle temperature. Based on the results from statistical processing of experimental data (Fig. 5a), we obtained the approximation expression for this constant in the following form:

$$k^r_{NO_x} = 1400\exp[-87000/(RT_s)]. \qquad (11)$$

The value of activation energy in (11) is close to that obtained in [10] for NO reduced on coke (82 kJ/mol).

The experiments for firing coals under steady conditions were carried out on a circulating fluidized bed (CFB) setup comprising a reactor 0.14 m in diameter and 5.6 m in height, a TsN-15 cyclone with a diameter of 250 mm for returning entrained particles, a TsN-15 cyclone 180 mm in diameter serving as the second stage of purification, and a fuel feed and entrainment return system. The reactor channel made of heat-resistant steel was either thermally insulated over the entire height or had a water-cooled upper part. The experimental setup was also fitted with secondary-blast nozzles, ash drain devices, and devices for sampling bed material. The fuel was fed from the bin by means of a screw-type feeder. The following parameters were measured in the setup during the experiments: temperature along the channel height (upstream and downstream of the cyclones) in the entrainment return chutes, pressure drop over the

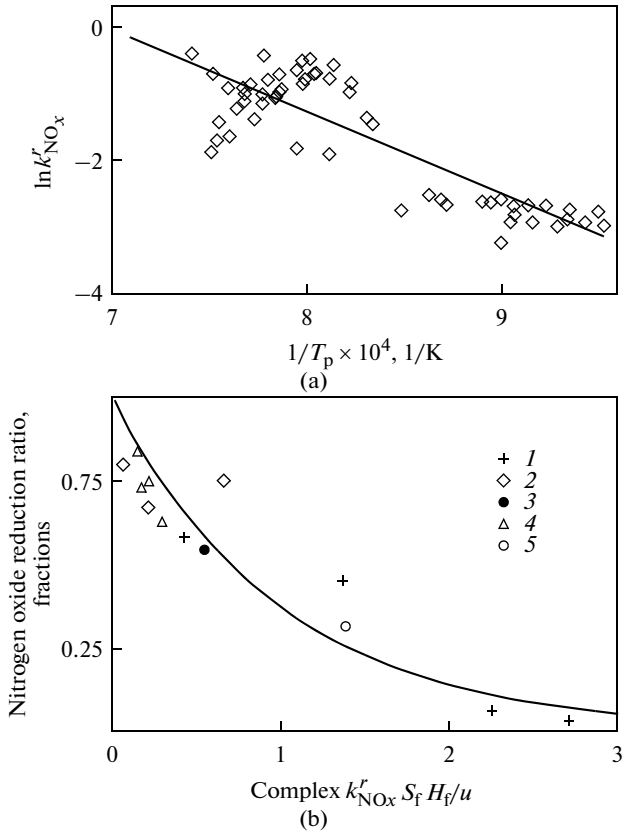

Fig. 5. Reaction rate constant of the nitrogen oxide reduction on carbon vs. the temperature (a) and comparison between the experimental data on the reduction of nitrogen oxides along the furnace height and calculated data (b). (*1*) Kuznetsk coal, (*2*) coal from the Moscow region, (*3*) anthracite, (*4*) shale, and (*5*) Berezovo coal.

reactor height, and flowrates of air, fuel, and natural gas used for kindling. The composition of combustion products was measured using continuous-duty gas analyzers.

The experimental data on distribution of nitrogen oxides over the reactor height obtained in the course of firing different coals were used in approximate calculations aimed at determining the change in the concentration of nitrogen oxides during their reduction in the CFB freeboard without taking into account the additional generation of NO_x in the bed due to combustion. The initial concentration of nitrogen oxides in the freeboard was taken equal to their concentration at the outlet from the bed according to the experimental data. The specific reaction surface of coke particles in the transport zone was calculated as for a flow of gases from the expression

$$S_f = \frac{6\overline{\rho}_{f.p} z_f}{\rho_c \delta_f},$$

where $\overline{\rho}_{f.p}$ is the average density of fuel particles in the flow, z_f is the concentration of combustible substances in entrainment, and δ_f is the diameter of fuel particles.

Figure 5b shows a comparison between the experimental data on the NO_x reduction ratio in the freeboard in firing different kinds of fuel on the CFB setup, which is defined as the ratio of measured concentrations at the furnace outlet to those at the bed outlet and the results of calculations carried out according to expression (10). In carrying out the calculations, we used the experimentally obtained values of particle sizes and concentrations in the freeboard for determining the specific surface of coke particles, and the corresponding flow temperatures for calculating the kinetic reaction constants. The noticeable scatter of the obtained values is due to a partial additional amount of nitrogen oxides generated during the combustion of volatiles in the freeboard and due to different reaction properties of fuel. Nonetheless, the general tendency, i.e., a growth of the nitrogen oxide reduction ratio with an increase in the concentration of circulating coke particles, is seen quite clearly.

We will consider two combustion and NO_x generation zones in calculating the generation of nitrogen oxides in a CFB furnace: a relatively dense fluidized bed and freeboard. The concentration of nitrogen oxides in the fluidized bed itself $C^{gen}_{NO_x}$ can be represented as the sum of concentrations of the nitrogen oxides generated from volatile compounds and from the nitrogen contained in coke residue, and calculated from expression (8). The decrease of the concentration of nitrogen oxides in the fluidized bed itself as a result of their reduction in the reaction with the coke residue carbon is calculated taking into account the obtained reduction constant (11)

$$\Delta C^{red}_{NO_x} = k^r_{NO_x} S H_{f.b}/u,$$

where $H_{f.b}$ is the fluidized bed full height.

Then, the expression for the concentration of nitrogen oxides at the bed outlet taking the reduction process into account becomes

$$C^*_{NO_x} = C^{gen}_{NO_x} - C^{red}_{NO_x}.$$

In the subsequent, we will take into account the generation of nitrogen oxides due to the combustion of circulating coke particles and their reduction according to the reaction C + NO_x, all along the furnace height. The change of nitrogen oxide concentration can in this case be described by an equation similar to (10) but with taking into account the specific reaction surface S_f in the transport zone

$$u\frac{dC_{NO_x}}{dh} = \nu_N k_N C^S_{O_2} S_f - \alpha^r_{NO_x} C_{NO_x} S_f. \qquad (12)$$

The initial concentration of nitrogen oxides in the transport zone is equal to the concentration of nitrogen oxides at the bed outlet (H_{tr} is the transport zone full height): $H_f = 0$, $C_{NO_x} = C^{f.b}_{NO_x}$. Here, the concentration of oxygen at the surface of coke particles is inter-

Table 3. Some operating parameters during the CFB combustion of Kuznetsk coals and Estonian shales

Parameter	Kuznetsk coal		Estonian shale		
Mode number	1	2	3	4	5
Bed temperature, °C	947	940	740	816	850
Gas velocity, m/s	7.40	6.10	5.95	7.05	6.90
Burning surface heat densities, MW/m^2	5.95	5.27	4.90	5.90	5.80
Concentration of combustible substances in the circulating material, %	43.60	55.70	1.98	1.35	2.10
Concentration of particles in the flow, kg/m^3	0.19	0.67	0.82	0.74	0.93
Total air excess factor	1.10	1.05	1.05	1.05	1.10
Primary air excess factor	0.77	0.68	0.93	0.64	0.73

related with the concentration of oxygen in the flow varying with height as follows:

$$C_{O_2}^S = \frac{C_{f.b}}{1 + k/\alpha_d} \exp\left(-\frac{\alpha_r S_f h}{u}\right). \quad (13)$$

Integrating Eq. (12) taking expression (13) into account, we obtain the expression for calculating the change of nitrogen oxide concentration in the CFB furnace freeboard in the form

$$C_{NO_x} = \frac{C_{NO_x}^{f.b}}{\exp\left(\frac{S_f h k_{NO_x}^r}{u}\right)} + \nu_N \left(\frac{k_N}{k}\right) \frac{C_{f.b}}{\frac{k_{NO_x}^r}{k_N} - 1} \frac{\exp\left[-\frac{\left(k_N - k_{NO_x}^r\right) S_f h}{u}\right] - 1}{\exp\left(\frac{S_f h k_{NO_x}^r}{u}\right)}. \quad (14)$$

The first summand in expression (14) characterizes the decrease of the concentration of nitrogen oxides generated in the fluidized bed resulting from their reduction in the freeboard. The second summand describes simultaneous generation and reduction of nitrogen oxides in the flow. An analysis of (14) has shown that the main component in the total yield of nitrogen oxides is determined by their generation in the fluidized bed. The fraction of nitrogen oxides generating in the freeboard does not exceed 20% of their total amount.

Calculations by formula (14) were carried out for the experimental conditions of firing Kuznetsk coal in a circulating fluidized bed (see Table 3 and Fig. 6) for moderate (mode 1) and intense (mode 2) circulation of coke particles and also for combustion of Estonian shale in CFB (Fig. 7). It can be seen from both the figures that the calculated and experimental data are in quite satisfactory agreement with each other.

The concentration of nitrogen oxides in the combustion products depends on the ratio between the amounts of primary and secondary air and on the overall value of air excess factor. In modes 1 and 2 the air excess factor $\alpha < 1$, which entails a decrease of nitrogen oxide concentration; the smaller the primary and secondary air excess factors, the more significant the reduction is.

The concentration of volatiles in the circulating material was around 40%. With the return of the entrainment's finely dispersed part organized at a height of around 4 m, the fuel intensely burned out in the furnace upper part, which is seen from a continuous growth of CO_2 concentration and drastic drop of NO_x concentration (see Fig. 6a) at a height of above 4 m. Particles of Kuznetsk coal do not have an ash skeleton, due to which a large amount of finely dispersed ash is produced during the combustion, which is poorly captured in the first-stage cyclone. Attempts to achieve isothermal combustion conditions were not met with success, because the concentration of particles in the flow had a low level and, accordingly, because the flow had a low specific heat in this mode.

In order to achieve a higher fuel burnout ratio and smaller concentration of volatiles in the entrainment in mode 2, the return of entrainment was organized both from the first cyclone through the flow-over device and from the second cyclone by means of an ejector through the secondary blast nozzles. Owing to a low reaction capacity of the coal, the concentration of combustible substances in the circulating material remained extremely high. With the return of entrainment organized from the second cyclone and with measures taken to achieve a better ash capturing ratio, it is possible to increase the concentration of circulat-

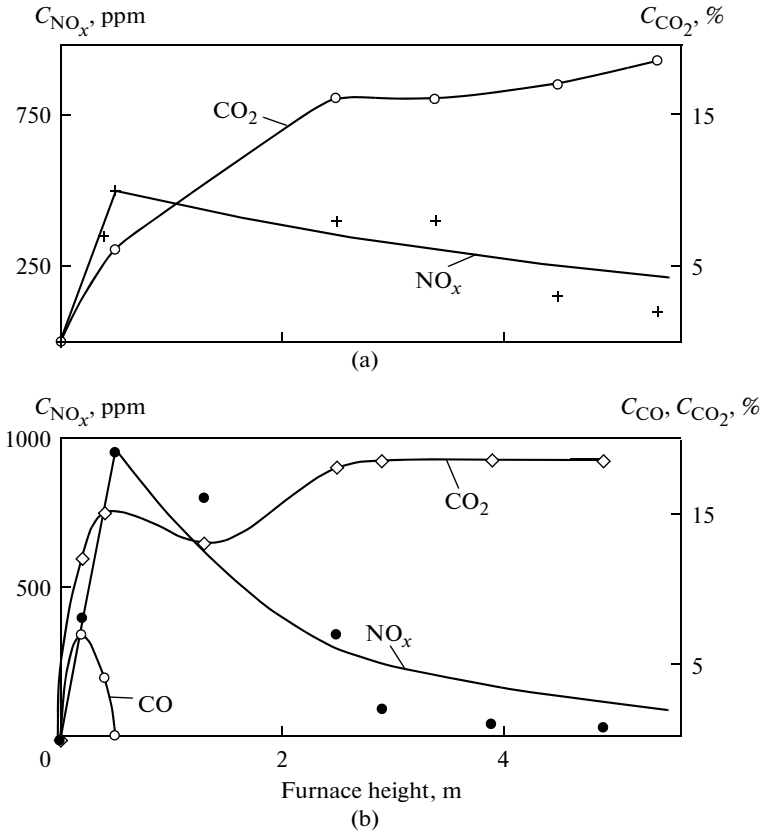

Fig. 6. Variation of nitrogen oxide concentration along the furnace height during the CFB combustion of Estonian shale in modes 1 (a) and 2 (b). The numbers of modes correspond to Table 3. The curves for NO_x represent the results of calculations using expression (14), and the points are for experimental data.

ing material (especially fine fractions), which leads to a noticeably higher nitrogen oxide reduction ratio.

In firing Estonian shale with the yield of volatiles equal to 90%, the concentration of combustible coke particles in the freeboard was insignificant; nonetheless, a drop of nitrogen oxide concentration from 150 to 100 ppm was observed.

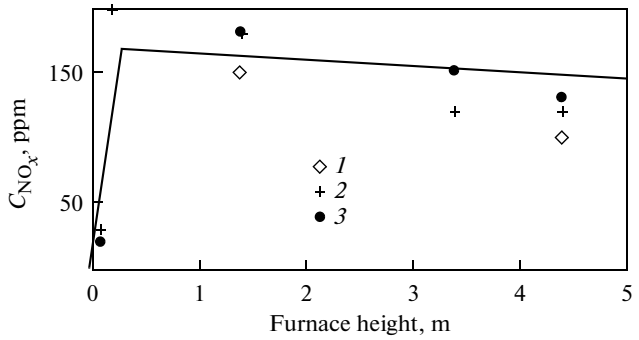

Fig. 7. Variation of gas concentration along the furnace height during the CFB combustion of Kuznetsk coals. The numbers of modes correspond to Table 3. The curves for NO_x represent the results of calculations using expression (14), and the points are for experimental data. Modes: (*1*) 3, (*2*) 4, and (*3*) 5.

CONCLUSIONS

(1) With solid kinds of fuel fired in a fluidized bed, fuel nitrogen oxides are produced during the combustion of both volatiles and coke residue, the concentrations of the produced NO and CO_2 being proportional to each other.

(2) Carbon and nitrogen oxidation reactions go simultaneously on the surface of coke residue particles. The quantity of generated nitrogen oxides is proportional to the content of nitrogen in coke residue and to the concentration of oxygen on the particle surface that is settled in the carbon oxidation reaction.

(3) The obtained dependence for the equilibrium constant of the resulting nitrogen oxide generation reaction during the combustion of volatiles in a fluidized bed on the bed temperature is in satisfactory agreement with the experimental data.

(4) The fact that nitrogen oxides are indeed reduced on the surface of coke particles has been confirmed by experiment, and the dependence for the rate constant of the equivalent nitrogen oxide reduction

reaction on the surface of particles on the particle temperature has been established.

(5) An expression for calculating the variation of nitrogen oxide concentration in the furnace freeboard has been obtained from mathematical simulation of the nitrogen oxide reduction process in a CFB furnace; the results of calculations carried out using this expression are in satisfactory agreement with the experimental data.

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